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HYDRATED CALCIUM PEROXIDES

de Forcrand

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ABSTRACT. Four experiments were conducted on hydrated calcium peroxides and the resulting fluid was tested for its separability with varying numbers of filters, and the characteristics of the precipitate were compared. Extensive conclusions on the results are discussed, as is the author's object of future research.

Hydrated calcium peroxides precipitate when hydrogen peroxide acts on solutions saturated with lime in exactly the same way as when barite or strontia is used.

/1308*

1. The effect of $1/2 \text{ H}_2\text{O}_2$ (1lit) on CaO (50lit). Temperature + 20° .
Final state in calorimeter

0.666 $\text{CaO}_{1.732}$ precipitate + 0.334 $\text{CaO}_{1.04}$ dissolved,

Heat liberated: 2. [Appears to be something missing--Tr.]

/1309

Thus, all corrections made: + 6cal, 877 for CaO_2 hydrated precipitate.

This substance forms an extremely fine and light powder which remains in suspension for a long while and which gives the liquid the appearance of milk. The liquid is clarified only slowly and with great difficulty after passing through several filters, and most of the precipitate remains attached to the paper pores. However, I have succeeded in collecting enough of it to perform an analysis, which yielded (after drying on porous plates)

$\text{CaO}_{1.842} + 2.31 \text{ H}_2\text{O}$.

All these characteristics -- the appearance and properties of the precipitate, its composition and formation heat -- all showed that we are dealing with a compound which is highly different from those obtained previously with BaO and SrO (+ 25 cal, 497 and + 26 cal, 576 and a hydration state of 8 to 9 H_2O).

In this particular case, these differences do not appear to be due to the more elevated temperature used in this test (+ 20°), because I carried out another series of tests at + 14° which yielded:

The final state: 0.647 $\text{CaO}_{1.754}$ precipitate + 0.353 $\text{CaO}_{1.04}$ dissolved.

Heat liberated: + 2cal, 940, or, after correction: +6cal, 899.

In these later tests, I immediately added dissolved H_2Cl_2 , which yielded

+25cal,128, or, after corrections: +21cal,425 for the effect of the dissolved H_2Cl_2 on the hydrated CaO_2 precipitate.

The total +6cal,899 + 21cal,425 = +28cal,324, a number which is very close to +27cal,960 (neutralization heat), which is a control.

II. The effect of H_2O (2lit,5) on CaO (50lit). Temperature 14° .

Final state: $0.908 \text{ CaO}_{1.96}$ precipitate + $0.092 \text{ CaO}_{2.4}$ dissolved.

Heat liberated: +6cal,163, or, after corrections: +6cal,668, a number which is identical with the preceding.

The hydration state should be the same, because the precipitate offers the same characteristics.

In one experiment, H_2Cl_2 dissolved yielded +22cal,062, or after corrections, +21cal,608 (6cal,668 + 21cal,608 = + 28cal,276).

III. The effect of $2\text{H}_2\text{O}_2$ (5lit) on CaO (50lit). Temperature + 14.5° .

Final state: $0.862 \text{ CaO}_{2.12}$ precipitate + $0.138 \text{ CaO}_{8.4}$ dissolved.

Heat liberated: +7cal,975, or +7cal,523 for $\text{CaO}_{2.12}$.

Thus, $\text{CaO}_{2.12}$ may be considered a mixture of dioxide and trioxide: $0.88 \text{ CaO}_2 + 0.12 \text{ CaO}_3$. In addition, because the preceding experiments yield +6cal,815 as an average for CaO_2 , the result is that the transformation of the CaO_2 into CaO_3 liberates +6cal,735, or about the same quantity of heat as is liberated when dissolved CaO is transformed into CaO_2 precipitate. The trioxide would therefore be more stable than in the case of barite.

The hydration state of the precipitate is, in addition, the same as that in preceding tests, specifically $2.07 \text{ H}_2\text{O}$.

IV. The effect of $3 \text{ H}_2\text{O}_2$ (7lit,5) on CaO (50lit). Temperature + 13° and + 14° .

Final state: $0.856 \text{ CaO}_{2.09}$ precipitate + $0.144 \text{ CaO}_{15.3}$ dissolved.

Here the phenomena change completely. The precipitate gathers rather quickly in the form of pearly lamella having the same appearance as hydrates of /1310 barium and strontium peroxide. It separates rapidly and completely, even with a single filter.

The heat liberated is also quite different: + 22cal,899, or, after corrections +24cal,666 for $\text{CaO}_{2.09}$. According to the preceding, approximately the same number can be allowed for a hydrated CaO_2 precipitate under the same conditions.

Finally, this substance, collected and dried in the same manner as the preceding substances were, has a composition of $\text{CaO}_{2.06} + 8.57 \text{H}_2\text{O}$. Thus, we again find the hydration state at 8 or 9 H_2O of the BaO_2 or SrO_2 precipitates.

As a control, H_2Cl_2 was immediately added after one of these experiments. I found + 4.732, or after corrections + 2cal,911 for $\text{CuO}_{2.09}$. The total +24.666 + 2.911 yields +27.577 (instead of +27.960).

Then I repeated the experiment with the same proportions of lime (1 mol) and hydrogen peroxide (3 mol), but operating at +20°, outside the calorimeter. The precipitate is pulverulent and filters quite slowly and incompletely with several filters, and its composition is $\text{CaO}_{1.94} + 2 \text{H}_2\text{O}$.

Finally, one last experiment was made taking $4\text{H}_2\text{O}_2$ for CaO and cooling the liquids in order to reduce them to the initial temperature of +10°. This experiment again yielded a precipitate in the form of pearly lamella which rapidly collected and were separated easily by a single filter, and which had a composition of $\text{CaO}_{2.02} + 7.62 \text{H}_2\text{O}$. This is the same substance as in the first experiments of IV.

From the preceding, it follows that:

1. Through a mixture of hydrogen peroxide solutions and bases, lime forms, as barite and strontia, precipitates of hydrated peroxides whose solubility is greater than that of strontium peroxides, but less than that of barium peroxides.
2. In three cases, the precipitates always carried down protoxide hydrate until the limit of 2 H_2O_2 molecules for one base molecule is reached, and that the dosage of the protoxide is greater when there is an excess of the base.
3. Between +10° and +16°, barite and strontia yield precipitates which retain approximately 8 to 9 H_2O , while the lime furnishes a dioxide with 2 H_2O , which is quite different in its appearance and its formation heat.
4. At the same temperatures, lime yields a dioxide of 8 or 9 H_2O when we take three or four H_2O_2 molecules for one base molecule.
5. When this change in the hydration state of the calcium dioxide depends solely on the temperature, then in operating at +20° the effect of 3 H_2O_2 yields the hydrate at 2 H_2O . The critical temperature would therefore be between 15° and 20°.
6. The three hydrates at 8 or 9 H_2O form and liberate a considerable amount of heat which is quite close:

$\text{CaO}_2 \dots\dots + 24.666$ $\text{BaO}_2 \dots\dots + 25.497$ $\text{SrO}_2 \dots\dots + 26.576$

7. The addition of 6 H_2O liquid to the $\text{CaO}_2 + 2 \text{H}_2\text{O}$ hydrate to change it into a $\text{CaO}_2 + 8 \text{H}_2\text{O}$ hydrate yields + 24.666 -6.815, or +17cal,851, or +3cal per water molecule if the first component is a dioxide hydrate and not a $\text{CaO}_2\text{H}_2 + \text{H}_2\text{O}_2$ combination, which I intend to investigate.

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